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END-OF-THE YEAR REPORT

PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT

for

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R&T PROJECT 4133002—12

SOLVATION DYNAMICS AND THE STRUCTURE IN ELECTROLYTES AND ELECTRODES

PRINCIPAL INVESTIGATOR
Dr. Lesser Blum

Physics Department
University of Puerto Rico
Rio Piedras, PR 00931-3343

OFFICE OF NAVAL RESEARCH
PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT

R&T Number: 4133002—12
Grant Number: N00014-90 J-1263
Grant Title: SOLVATION DYNAMICS AND THE STRUCTURE IN ELECTROLYTES AND ELECTRODES
Principal Investigator: Lesser Blum
Mailing Address:
Physics Department
University of Puerto Rico
Rio Piedras, PR 00931-3343
Phone Number: (809) 764-0000 xt 13576 Fax Number: (809) 763-3390
E-Mail: L_blum@upr1.upr.clu.edu

a. Number of papers submitted to refereed Journals, but not published: 14
b. Number of papers published in refereed Journals (list attached): 11
c. Number of books or chapters submitted, but not published: 2
d. Number of books or chapters published (list attached): 0
e. Number of printed technical reports & non refereed papers (list attached): 0
f. Number of patents filed: 0
g. Number of patents granted: 0
h. Number of invited presentations at workshops or professional society meetings : 8
i. Number of presentations at workshops or professional society meetings : 3
j. Honors/Awards/Prizes for contract /grant employees (list attached): 4
k. Total number of graduate students and post-doctoral associates supported at least 25% during this period:
Graduate students: 2
Post-Doctoral associates: 2
including the number of,
Female graduate students: 0
Female Post-Doctoral associates: 0
the number of,
Minority Graduate Students: 1
Minority Post-Doctoral associates: 2
and the number of,
Asian Graduate Students: 0

Asian Post-Doctoral associates: 0

I. Other funding:

1. NSF Chemistry

Molecular Ionic Solutions in Water

$147,000.- (1995-1998)

2. NSF-Epscor

Materials Science Research Center

$50,000.- (1995-1997) Under no-cost extension

PART I

a. Papers Submitted

1. L. Blum and W. R. Fawcett, DIELECTRIC BEHAVIOUR OF OF POLAR POLARIZABLE SOLVENTS IN GENERIC MEAN SPHERICAL APPROXIMATIONS: THE KIRKWOOD gK FACTOR J. Phys. Chem., (1996).

2. L. Blum, Dale A. Huckaby and M. Legault, PHASE TRANSITIONS AT ELECTRODE INTERFACES, Electrochim. Acta (In Press)

3. M. D. Legault, L. Blum and Dale A. Huckaby, AN EXTENDED HARD HEXAGON MODEL FOR COPPER UPD ON Au(111), J. Electroanal. Chem.

4. L. Blum , Dale A. Huckaby and M. Legault, COMMENT ON 'ELECTROCHEMICAL DEPOSITION OF COPPER ON A GOLD ELECTRODE IN SULFURIC ACID: RESOLUTION OF THE INTERFACIAL STRUCUTRE', Phys. Rev. Letters, submitted.

5. J.P. Simonin and L. Blum, DEPARTURES FROM IDEALITY IN PURE IONIC SOLUTIONS USING THE MEAN SPHERICAL APPROXIMATION, J. Chem. Soc. Faraday (in press).

6. J.P. Simonin, L. Blum and P. Turq, THERMODYNAMICS OF REAL IONIC SOLUTIONS IN THE MEAN SPHERICAL APPROXIMATION: SIMPLE SALTS IN THE PRIMITIVE MODEL J. Phys. Chem.

7. S. Durand-Vidal , P. Turq , O. Bernard, C. Treiner and L. Blum , NEW PERSPECTIVES IN TRANSPORT PHENOMENA IN ELECTROLYTE SOLUTIONS, Physica A (submitted).

8. J. N. Herrera and L. Blum, EQUATION OF STATE FOR A CHARGED COLLOIDAL SYSTEM, Physica A (submitted).

9. O. Bernard and L. Blum, BINDING MEAN SPHERICAL APPROXIMATION FOR PAIRING IONS: THE BIMSA-EXP APPROXIMATION AND THERMODYNAMICS, J. Chem. Phys., (1996).

10. L. Blum and L. Degrève, MONTE CARLO STUDY OF ANALYTIC POTENTIALS FOR WATER Mol. Phys. (in Press).

11. L. Degrève and L. Blum, ANALYTIC POTENTIAL FOR WATER: A MONTE CARLO STUDY, Physica A (in Press).

12. Yu. V. Kalyuzhnyi, L. Blum, M. F. Holovko and I. A. Protsykevytch PRIMITIVE MODEL FOR HIGHLY ASYMMETRIC ELECTROLYTES: ASSOCIATIVE MEAN SPHERICAL APPROXIMATION J. Chem. Phys. (submitted)

13. I. A. Protsykevytch, Yu. V. Kalyuzhnyi,M. F. Holovko and L.Blum, GENERAL SOLUTION OF THE POLYMER MSA FOR THE TOTALLY FLEXIBLE TWO POINT ELECTROLYTE MODEL, J. Stat. Phys. (Submitted).

14. L. Blum, Yu. V. Kalyuzhnyi, O. Bernard and J. N. Herrera, STICKY CHARGED SPHERES IN THE MEAN SPHERICAL APPROXIMATION: A MODEL FOR COLLOIDS AND POLYELECTROLYTES, J. Physics Cond. Matter (Submitted)

b. Papers Published in Refereed Journals

1. O. Pizio and L. Blum, ANALYTIC SOLUTION OF THE MEAN SPHERICAL APPROXIMATION FOR A DIPOLAR HARD SPHERE FLUID WITH INTRACORE ANISOTROPIC STICKY INTERACTIONS, Phys. Revs. E. , **52** 572 (1995).

2. L. Blum and F. Vericat AN ANALYTICAL MODEL OF WATER WITH STICKY SPHERES OF TETRAHEDRAL SYMMETRY Mol. Phys. **86** 809 (1995), issue commemorating the 60th birthday of Douglas Henderson.

3. L. Blum and F. Vericat, WATER AS HARD-SPHERES WITH A STICKY POTENTIAL OF TETRAHEDRAL SYMMETRY J. Phys. Chem., **100** 1197 (1996).

4. P. Turq, O. Bernard, W. Kunz and L. Blum, TRANSPORT IN ELECTROLYTES USING THE MEAN SPHERICAL APPROXIMATION: ELECTRICAL CONDUCTANCE AND SELF DIFFUSION COEFICIENT AS A FUNCTION OF CONCETRATION IN SOLUTIONS, in *Complex Fluids* Proceedings of the Sitges Conference, L. Garrido (Ed.) , Lecture Series in Physics **415** Springer Verlag, Berlin (1992).

5. A. Chhih, P. Turq, O. Bernard, J. M. G. Barthel and L. Blum, TRANSPORT COEFICIENTS AND APPARENT CHARGES IN CONCETRATED ELECTROLYTE SOLUTIONS: EQUATIONS FOR PRACTICAL USE, Ber. Bunsenges, **98** 1516 (1994).

6. P. Turq, L. Blum, O. Bernard and W. Kunz, CONDUCTANCE IN ASSOCIATING ELECTROLYTES USING THE MSA, J. Phys. Chem., **99** 822 (1995).

7. L. Blum and O. Bernard, THE GENERAL SOLUTION OF THE ASSOCIATING MEAN SPHERICAL APPROXIMATION FOR DIMERIZING IONS, J. Statistical Phys., **79** 569 (1995).

8. M. Legault, L. Blum and D. A. Huckaby, A MEAN FIELD TREATMENT OF THE HARD HEXAGON INTERACTIONS IN THE HB MODEL, 2^{nd} W. Schmickler, ed. *Ulmer Elektrochemische Tage*, p 201, Universitätsverlag Ulm, GmbH (1995).

9. D. A. Huckaby and L.Blum, A MODEL FOR THE UNDERPOTENTIAL DEPOSITION OF METALS, in *Diffusion Processes: Experiment, Theory , Simulations*, A. Pekalski, Editor, Springer Verlag, Berlin (1994).

10. D. A. Huckaby and L.Blum, RIGOROUS ANALYSIS OF LOW TEMPERATURE PHASES IN A MODEL FOR THE UNDERPOTENTIAL DEPOSITION COPPER ON THE (111) SURFACE OF GOLD IN THE PRESENCE OF BISULFATE, Langmuir, 11 4583 (1995).

11. L. Blum, M. F. Holovko and I.A. Protsykevych, A SOLUTION OF THE MULTIPLE BINDING MEAN SPHERICAL APPROXIMATION FOR IONIC MIXTURES J. Statistical Phys., 84 191 (1996).

c. Books in Print

1. Lesser Blum (U. of Puerto Rico) and Sow-Hsin Chen (MIT) *COLLOID AND INTERFACE SCIENCE: TRENDS AND APPLICATIONS*, Conference Proceedings, published by Elsevier, Amsterdam, (In preparation, 1996).

2. M. D. Legault, *Statistical Mechanical Models of the Adsorption of Copper onto Gold(111) in the Presence of Sulfuric Acid*, Thesis, University of Puerto Rico (1996).

d. Books Published

None

e. Technical Reports

1. L. Blum and W. R. Fawcett, DIELECTRIC BEHAVIOUR OF OF POLAR POLARIZABLE SOLVENTS IN GENERIC MEAN SPHERICAL APPROXIMATIONS: THE KIRKWOOD gK FACTOR J. Phys. Chem., (1996).

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10. L. Blum and L. Degrève, MONTE CARLO STUDY OF ANALYTIC POTENTIALS FOR WATER Mol. Phys. (in Press).

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13. L. Blum, Yu. V. Kalyuzhnyi, O. Bernard and J. N. Herrera, STICKY CHARGED SPHERES IN THE MEAN SPHERICAL APPROXIMATION: A MODEL FOR COLLOIDS AND POLYELECTROLYTES, J. Physics Cond. Matter (Submitted)

f. Patents filed:

None.

h. Invited Conferences

1. University of Regensburg, a series of 4 lectures on *Theoretical Foundations of Electrochemistry*, July 7,14,21 and 28 of 1995, sponsored by the H.J.Vielberth Foundation.

2. University of Regensburg, THE STRUCTURE OF THE METAL-ELECTROLYTE INTERFACE, July 24, 1996.

3. Snowdonia Conference on the Dynamics and Structure
at Electrified Interfaces, Harlech, England July 17-21, 1995.
Member of International Advisory Committee.Invited Speaker.

4. A COMPREHENSIVE MODEL FOR THE UPD OF Cu ONTO Au(111), invited contribution to the Symposium *Electron spectroscopy of the Solid Liquid Electrochemical Interface*, PACIFCHEM, Honolulu, Hawaii, Dec. 15, 1995.

5. MONTE CARLO STUDY OF ANALYTIC POTENTIALS OF WATER, invited contribution to the Symposium *Solvation Dynamics: From ions to Proteins*, PACIFCHEM, Honolulu, Hawaii, Dec. 15, 1995.

6. ANALYTICAL SOLUTION OF THE BINDING MEAN SPHERICAL APPROXIMATION FOR COLLOIDS AND POLYMERS, invited contribution to the *Workshop on Current Problems in Complex Fluids*, Oaxaca, Mexico, January 6, 1996.

7. *Topics in Modern electrochemistry* , a 6 lecture course given at the University of Sao Paulo, Riberao Preto, Brazil, March 25- April 18, 1996.

8. CLUSTER VARIATION STUDY OF THE UNDERPOTENTIAL DEPOSITION OF COPPER ONTO GOLD(111), invited contribution to the *Sixth International Symposium on Electrode Processes*, 186th Meeting of the Electrochemical Society, Los Angeles, May 7, 1996.

i. Topical Conferences

1. STRUCTURAL MODEL OF WATER, Rutgers University, Chemistry Department, October 11, 1995.

2. MOLECULAR ORIENTATION AT ELECTRODE SURFACES, Penn State University Chemistry Department, October 12, 1996.

3. PHASE TRANSITIONS AT ELECTRODES: Cu/Au(111) UPD AS THE EXAMPLE, Institute for Physical Chemistry and Electrochemistry, University of Sao Paulo, Sao Carlos, Brazil.

j. Honors/Awards/Prizes

1. L. Blum, SPA, Scientific Productivity Award by the University of Puerto Rico, 1994.

2. Member, Editorial Commitee of Physica (A) from 1996, for 3 years.

3. *Puerto Rico Workshop on Problems in Mathematical Physics of Coulomb Systems,* March 14-16 at the Rio Piedras Campus of the University of Puerto Rico. Organizers: Lesser Blum and Joel L. Lebowitz.

4. Co-Organizer, with P. Turq and M. Marechal, CECAM Workshop on *Models and Computer Simulations of Electrokinetic Phenomena,* Lyon, France, July 26-29 (1996).

PART II

a. Principal Investigator

Lesser BLUM

b. Current Telephone Numbers

Lesser Blum (787) 764-0000 xt 13576

c. Cognizant Scientific Officer

Robert J.Nowak

d. Description of Project.

The underpotential deposition (UPD) of metals, such as copper, silver, lead, bismuth onto other metals such as gold, platinum has been the subject of much research recently. These processes provide unique opportunities to study the structure and transformations occuring at metal/electrolyte interfaces: This is so because in the UPD sharp transformations (phase transitions) occur that can be measured by an array of techniques which include unambiguous X-ray based in situ structural analysis, which was demonstrated in previous periods of this project.

We have also developed simple but reliable theoretical tools for the understanding of the relations between structure and transformations in the UPD process, and in particular the role of the anions, using models of classical interactions. We have been successful in predicting in 1991 and 1994 the stucture of the 2/3 cverage phase in the case of the underpotential deposition (UPD) of copper on gold (111) in the presence of sulphuric acid, recently published by Toney et al.

In our theory we have treated, for reasons of convenience, the two spikes in the Cu/Au(111) in the presence of Sulfate ions as separate events. We did treat the two transformations as two independent events in which only two components where present. More recently, we have developed a theory in which three components the sulfate, copper, and the solvent are treated at the same level. The new theory, which we call the extended hexagon model, accounts for the broad foot region of the voltammogram, the adsorption isotherm and of the quartz crystal microbalance curve. In the new model we use the Guggenheim- McGlashan method to account for the long range interactions between the sulfate ions adsorbed on the gold surface. The exclusion effects of the hard hexagon play a very important role in shaping the voltammogram, and indeed, by proper adjustement of the interaction parameters, we obtain shapes that correspond to other UPD voltmmograms, such as the Cu/Au(111) in the presence of Br.

Our fruitful collaboration with W.R.Fawcett on the question of simple analytical theories for ionic solvation in water and other solvents will be pursued. We have made much progress in developing a suitable model of water that can be treated analytically, and that at the same time

fits the known structural and thermodynamic properties of bulk water, such as the pair distribution functions for the oxygen-oxygen, oxygen-hydrogen and hydrogen-hydrogen correlation functions obtained.

The new analytical explicit solution of the sticky tetrahedral water model will permit extensions of the dipole model to realistic situations. This model compares surprisingly well with the best structure of liquid water from neutrons as obtained by Soper and Silver. We hope to be able to obtain simple relations between the structure forming parameters of Blum and Fawcett and the tetrahedral hydrogen bonding parameters of the recent work of Blum, Degreve and Vericat. The dynamic and chemical association effects have been studied with simple models (MSA), and excellent agreement to experiment.

f. Summary of Plans

The study of the phase transitions in the UPD process will be pursued using the sticky site model (SSM) developed previously. We have recently been successful in formulating a version of the cluster variation method for the extended hexagon model (CVM-EHM) in which the phase behaviour of the adsorbed monolayer can be computed in terms of ionic activities and effective interaction parameters: for example, en the case of Cu/Au(111) /SO_4 it will be the Cu-Cu , Cu-SO_4, and the SO_4-SO_4 effective interactions, as well as their activities. In our present investigation we are fitting these parameters to the experimental voltammogramms and adsorption isotherms. The investigation of the critical parameters of these isotherms will allow us prediction of the conditions for the presence or absence of phases such as the 2/3 coverage phase in this case. We will aim at constructing a theory in which the ionic interaction parameters will determine the shape and number of transitions in the voltammogram.

- We will develop a detailed theory for the underpotential deposition (UPD) of of Cu/Au(111) in the presence of selected anions, in terms of ion-metal and ion-ion interactions. The two major ingredients are a modified Guggenheim and McGlashan cluster variation method, and an extension of the Baxter hard hexagon model to attractive and repulsive hexagons using the Widom theorem. Potential shifts and kinetic aspects pertaining to the film formation will be studied. This will be applied to other cases, such as Cu/Pt(111), in which the voltammogram shows one spike for low sulfuric acid concentrations , and two for high concentrations, and to other cases which involve even more complicated interactions. The immediate goal is to define lateral and adsorption interaction parameters, with which we can predict the sequence of phase formation. The long range idea is to establish empirical rules (somehow reminiscent to the Woodward-Hoffman rules) for the formation of ordered structures on metal surfaces.

- Study the voltammogram shifts of the peaks, in their relation to the overall kinetic reaction constants.

- Study simple quantum mechanical models of adsorption. The basic idea is to use tight binding methods adapted to study monolayer adsorption of various kinds. Studies are currently done collaboration with Profs. L. Foseca and F. Zypman of our University.

- Study of the STM image theoretically. We will perform a theoretical calculation of the electronic structure of the honeycomb intermediate step of our problem, to explain the apparent contradiction in the STM result of Itaya, which yields 1/3 of copper coverage

and our theory, which requires 2/3 of a Cu monolayer. This will be done in collaboration with Profs. L. Foseca and F. Zypman of our University and the Centre de Calcul of the University of Montreal.

We plan to pursue the studies on the structure and dynamics of the phase transformations at electrode interfaces and the solvation dynamics and structure in relation to the Marcus theory:

In the problem of dynamics of solvation we plan to :

- Use the new analytical explicit solution of the sticky tetrahedral water model to study the low frequency response of the dielectric constant and solvation energy. We will find simple relations between the structure forming parameters of Blum and Fawcett and the tetrahedral hydrogen bonding parameters of the recent work of Blum and Vericat.
- Develop the quenched-annealed formalism to study the high frequency limit of a system of spheres with a permanent dipole moment and polarizability. This approach was never used when studying the optical dielectric limits of the solvation energies, an important parameter in Marcus theory.
- Use the microfield formulation developed some years ago to compute the van Hove response functions of a molecular solvent in the high and low frequency limits.

We will continue this work in the framework of the collaboration with Prof. R.W. Fawcett to study solvent effects in electrokinetics.

g. Graduate Students

1. Marc Legault (UPR)
2. Esov Velasquez (UPR)

h. Post-Doctoral

1. D.Q. Wei
2. F. Vericat